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(54) Title: PROCESS FOR PREPARING CUMENE WHICH IS USED IN THE PREPARATION OF PHENOL

(57) Abstract: The invention relates to a process for the preparation of cumene by reacting isopropanol or a mixture of isopropanol and propene with benzene in presence of a  $\beta$ -zeolite catalyst having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than 10:1 that can be integrated in a process for preparing phenol, which comprises the steps: I. preparation of cumene as described above, II. oxidation of cumene to cumene hydroperoxide, III. acid-catalyzed cleavage of cumene hydroperoxide to give phenol and acetone and IV. hydrogenation of acetone to form isopropanol. In the reaction of isopropanol with benzene, propene is formed by dehydration of isopropanol simultaneously with the alkylation of benzene to cumene by means of isopropanol and the propene formed is likewise used for the alkylation of benzene to cumene. Formation of n-propylbenzene in this process step according to the invention is barely observed or is in the range below 150 wppm. The  $\beta$ -zeolite catalyst having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than 10:1 exhibits an increased activity in the alkylation of benzene and leads to a higher selectivity in the alkylation, so that the yield in the overall process for preparing phenol can be improved compared to conventional processes.

PROCESS FOR PREPARING CUMENE WHICH IS USED IN THE PREPARATION OF PHENOL

The present invention relates to a process for preparing phenols.

5

Phenol is an important industrial chemical which is required for the preparation of phenol resins,  $\epsilon$ -caprolactam, bisphenol A, adipic acid, alkylphenols, aniline, chlorophenols, picric acid, plasticizers, antioxidants and similar compounds. Phenol  
10 is usually prepared from cumene by the Hock process.

In the preparation of phenol from cumene by the Hock phenol synthesis, acetone is formed as a coproduct. Since the commercial demand for phenol is frequently very different from  
15 that of acetone, attempts have been made for a long time to find ways of generating downstream products from acetone obtained so as to avoid dependence on the acetone market alone.

A possible downstream product of acetone is isopropanol which  
20 can be processed to give ethers such as diisopropyl ether and tert-butyl isopropyl ether.

The conversion of acetone into isopropanol is generally achieved by catalytic hydrogenation. For the production of  
25 isopropanol ethers, combination processes involving hydrogenation and etherification are usually employed. Thus, EP 0 694 518, EP 0 665 207, EP 0 652 200 and EP 0 661 257 teach processes for the preparation of various isopropyl ethers. In these patent applications, two process steps frequently proceed  
30 in direct succession: namely the catalytic hydrogenation of an acetone-containing, liquid phase and the etherification of the isopropanol obtained in this way over acid catalyst systems. The isopropanol mixture is not worked up after the catalytic hydrogenation.

In addition, EP 0 665 207 teaches a single-stage process in which the hydrogenation and etherification occur in one reactor.

5 In these processes, which are designed for the preparation of isopropyl ethers, isolation of the isopropanol after hydrogenation of the acetone is very costly because of by-product formation.

10 Although the preparation of downstream products from acetone enables direct dependence on the acetone market to be avoided, there continues to be a dependence on the market situation for the downstream products. It would therefore be desirable to find a way of producing phenol in which no coproduct is formed.

15

EP 0 371 738 describes a process for preparing phenol in which the acetone formed in the cleavage of cumene hydroperoxide is hydrogenated to give isopropanol, this isopropanol is used for the alkylation of benzene to give cumene and the cumene is  
20 reoxidized to cumene hydroperoxide by means of oxygen. Thus, this process in principle produces phenol from benzene and oxygen. In a preferred embodiment disclosed in EP 0 371 738 a proton-exchanged Y type skeleton zeolite having a ratio of silica to alumina of from 4:1 to less than 10:1 is used in the  
25 alkylation step.

In this process, the alkylation of benzene is carried out using isopropanol and/or propene as alkylating reagent in the liquid phase. It has been observed that the yield of alkylation  
30 products is decreased by a dehydration reaction of isopropanol which proceeds simultaneously. In addition, the authors have observed an alkylation of benzene by dissolved propene and, on the basis of their observation, only a very low yield of cumene can be achieved. The use of a circulation apparatus in which  
35 the olefin-containing stream is continually recycled allows the

authors to achieve selective consumption of the isopropanol feed for the alkylation of benzene. This procedure minimizes the proportion of isopropanol which is dehydrated to the olefin and thus is no longer available for the actual alkylation.

5

The alkylation of benzene to cumene has been examined in more detail in the two Japanese published specifications JP 11-035497 and JP 11-035498. Thus, JP 11-035498 is concerned with the problem of the alkylation of benzene by means of isopropanol producing water which forms an azeotrope with benzene and isopropanol and thus makes the separation of the reaction products difficult. As a solution, it is proposed that the water formed be removed from the reaction mixture prior to separation of unreacted benzene from the reaction mixture. JP 11-035497 is concerned with the problem of the alkylation of benzene by means of isopropanol forming diisopropyl ether which makes the work-up and separation of the reaction products difficult. As a solution, it is proposed that the reaction of benzene and isopropanol be carried out in the presence of water and a zeolite.

US 5,160,497 discloses a phenol production process wherein benzene is reacted with a feedstock comprising propene and isopropanol by contacting a dealuminized Y zeolite with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio ranging from 8 to 70. Cumene obtained in this step is oxidized to yield cumyl hydroperoxide, said hydroperoxide is cleaved to obtain a mixture of phenol and acetone and said acetone is hydrogenated to yield isopropanol that is recycled to the alkylation step. Although the examples show that the catalyst is useful for alkylation there is nevertheless the desire to increase conversion and selectivity in respect to cumene in the alkylation step.

In view of the known prior art, it is an object of the present invention to provide a process for preparing cumene by alkylation of benzene with isopropanol, in which, despite

dehydration of isopropanol to propene, a more complete conversion of isopropanol, a higher conversion and a higher selectivity in respect of cumene and lower n-propylbenzene formation in the alkylation step, compared to conventional  
5 processes, are achieved and which can be easily integrated in a process for preparing phenol comprising the steps

- I. preparation of cumene by reaction of isopropanol or a mixture of isopropanol and propene with benzene,
- II. oxidation of cumene to cumene hydroperoxide,
- 10 III. acid-catalyzed cleavage of cumene hydroperoxide to give phenol and acetone and
- IV. hydrogenation of acetone to form isopropanol.

This object has been attained by a process for the preparation  
15 of cumene by reacting isopropanol or a mixture of isopropanol and propene with benzene in presence of a  $\beta$ -zeolite catalyst having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than 10:1.

Another aspect of the present invention is a process for  
20 preparing phenol from benzene, which comprises the steps

- I. preparation of cumene by reaction of isopropanol or a mixture of isopropanol and propene with benzene,
  - II. oxidation of cumene to cumene hydroperoxide,
  - III. acid-catalyzed cleavage of cumene hydroperoxide to give  
25 phenol and acetone and
  - IV. hydrogenation of acetone to form isopropanol,
- wherein, cumene is prepared in accordance with the above described process.

30 A further aspect of the present invention is a process for the hydrogenation of acetone to isopropanol in at least two process steps, wherein the acetone used is crude acetone.

Sill a further aspect of the present invention is the use of a  
35  $\beta$ -zeolite catalyst having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than

10:1 in the alkylation of benzene with isopropanol or a mixture of isopropanol and propene.

It has surprisingly been found that a process for preparing phenol in which cumene is prepared by reaction of isopropanol with benzene over a  $\beta$ -zeolite catalyst having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than 10:1, propene is formed by dehydration of isopropanol simultaneously with the alkylation of benzene to cumene by means of isopropanol and the propene formed is likewise used for the alkylation of benzene to cumene makes the preparation of cumene simpler and makes it possible to achieve a more complete conversion of isopropanol and a higher selectivity of the reaction in respect of cumene and reduced formation of n-propylbenzene, so that a higher selectivity can be achieved in the preparation of phenol.

The process of the present invention makes it possible to prepare phenol without the coproduct acetone or downstream products of acetone which do not lead to cumene or isopropanol being formed. The economics of the preparation of phenol is thus only dependent on the achievable sales prices for phenol.

In addition, the process of the invention has the advantage that the dehydration of isopropanol to propene, the alkylation of benzene to cumene by means of the propene formed and the alkylation of benzene to cumene by means of isopropanol can occur simultaneously over  $\beta$  zeolites having  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratios of greater than 10:1 in one synthesis step. The last-named subreactions lead to the desired cumene in higher conversions and with a higher selectivity compared to processes which have been customary hitherto. A further advantage of the process of the invention is that when the reaction is carried out at the same temperature, significantly less n-propylbenzene is formed than in conventional processes. Since n-propylbenzene cannot be used further in an economically feasible way, the avoidance of

relatively large amounts of n-propylbenzene allows considerable costs for the reprocessing of this material to be saved. Furthermore, the suppression of the formation of n-propylbenzene increases the selectivity of the reaction in  
5 respect of the preparation of cumene.

A further advantage of the process of the invention is that isopropanol which can be used for the alkylation can be prepared by hydrogenation of crude acetone. The ability to  
10 hydrogenate crude acetone directly makes it possible to omit complicated work-up or purification of crude acetone obtained, for example, in the cleavage of cumene hydroperoxide. The outlay in terms of apparatus and thus the costs in the overall process for preparing phenol can be further reduced in this  
15 way.

The process of the invention for preparing phenol from benzene comprises the four process steps

- 20 I. preparation of cumene by reaction of isopropanol or a mixture of isopropanol and propene with benzene over an acid catalyst,
- II. oxidation of cumene to cumene hydroperoxide,
- III. acid-catalyzed cleavage of cumene hydroperoxide to give  
25 phenol and acetone and
- IV. hydrogenation of acetone to form isopropanol.

The process of the invention is described below by way of example, without being restricted to the description.  
30

A description of the individual processes and process steps which are substeps of the process of the invention will firstly be given.

35 Step I: Alkylation of benzene to cumene by means of isopropanol

In this first step, cumene is prepared by reacting isopropanol or a mixture of isopropanol and propene with benzene. The conversion of benzene into cumene is based on an alkylation of benzene by means of an alkylating reagent. Both isopropanol, which is fed into the reactor, and propene, which can be included into the feed stream and/or can be formed in a dehydration reaction which proceeds simultaneously, serve as alkylating reagents. In the process of the invention for preparing cumene by reaction of isopropanol with benzene contacting a  $\beta$  zeolite having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than 10:1 as catalyst or the process step according to the invention, propene is formed by dehydration of isopropanol simultaneously with the alkylation of benzene to cumene by means of isopropanol and the propene formed and or included in the feed stream is likewise used for the alkylation. Thus, in principle, three subreactions proceed, preferably simultaneously, in the process of the invention. One reaction is the alkylation of benzene to cumene by means of isopropanol. The second reaction is the dehydration of isopropanol to propene and the third reaction is the alkylation of benzene to cumene by means of the propene.

According to the invention,  $\beta$  zeolites having an  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio of greater than 10:1 are used as catalyst in the alkylation step. Very particular preference is given to using  $\beta$  zeolite catalysts having an  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio of from 20:1 to 200:1, preferably greater than 70:1 to 200:1. Due to hydrophobicity of the catalysts resulting from the high modulus, i.e. the high  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio, the acid centers are not fully occupied by the water formed in the reactions. The actual alkylation reaction, which proceeds simultaneously with the dehydration, is thus not brought to a halt. However, partial occupation of the zeolite surface by the water formed in the reaction achieves a acidity-modifying effect explained in more detail below.

The alkylation reactions and the simultaneous dehydration reaction can be carried out in one or more reactors. The alkylation reactions and the simultaneous dehydration reaction are preferably carried out in a stirred tank reactor, a fixed-bed reactor or a trickle-bed reactor. Moving, suspended or fixed catalysts can be used in the reactor or reactors. Preference is given to using reactors having a fixed catalyst bed charged with suitable shaped bodies, e.g. appropriate extrudates, of the catalyst used.

10

The starting materials benzene and isopropanol and optionally propene are introduced into the reactor in liquid and/or gaseous form, preferably liquid form. The feed stream to the reactor preferably has a molar ratio of benzene to isopropanol of greater than 1:1, particularly preferably from 3:1 to 10:1. As starting materials fed in, it is possible to use not only pure starting compounds but also compounds containing impurities. The isopropanol used as starting material preferably has a water content of less than 10% by weight, preferably less than 5%.

In the reactor, the reaction of isopropanol with benzene to form cumene, the dehydration reaction which proceeds simultaneously and the reaction of the propene formed or added with benzene to give cumene, i.e. the alkylation reactions, are carried out at a reaction temperature of from 100 to 300°C. The reactor preferably has a temperature gradient which is set so that the reaction mixture in the vicinity of the reactor inlet has a temperature of from 150 to 200°C and that in the vicinity of the reactor outlet has a temperature of from 250 to 300°C. The reactions are preferably carried out at a pressure of from 10 to 100 bar abs, preferably from 20 to 60 bar abs. Propene is generated in the reactor by the simultaneous isopropanol dehydration. The liquid phase has to be brought into intimate contact with the catalyst so that the alkylation reactions can

proceed. This can be ensured, for example when using a trickle-bed reactor, by using high linear velocities of the liquid phases in the reactor, preferably greater than 30 m/h.

5 The ratio of isopropanol used to benzene and/or the amount of recirculated product influences the water content in the reactor. The water content in turn influences the acidity of the catalyst. If a separate aqueous phase is formed, this has to be intensively dispersed in the reactor. This can be  
10 achieved by high linear velocities. The acidity of the catalyst is modified by the water formed in the reaction. According to a preferred embodiment of the present invention the water content of the total feed including optionally recirculated product into the alkylation reactor is maintained to be 5 wt-% at the  
15 most. Preferred water contents range from 0.1 to 5 wt-%, more preferred from 0.5 to 4.5 wt-%. This novel measure, which results in an acidity-modified catalyst, makes it possible to minimize the formation of n-propylbenzene, a product of a secondary reaction in the alkylation. The n-propylbenzene  
20 content of the reaction mixture or reactor output is usually less than 300 wppm, preferably less than 150 wppm, when carrying out the process of the invention.

The process of the invention for preparing cumene by reaction  
25 of isopropanol with benzene in presence of the catalyst of the present invention makes it possible to prepare cumene in one synthesis step. According to the invention, isopropanol is dehydrated to propene in the liquid phase in the presence of the catalyst of the present invention and at the same time  
30 benzene is alkylated by means of isopropanol to form cumene. Likewise, the propene formed as an intermediate or that is present in the feed, which can be partly present in a gas phase, reacts simultaneously with the benzene present in the reaction mixture to give the desired cumene. All subreactions  
35 are favored or accelerated by the presence of the  $\beta$  zeolite

catalyst.

The process of the invention or substeps thereof can be carried out continuously or batchwise. The simultaneous reactions of alkylation and dehydration are preferably carried out continuously. When the process of the invention is carried out batchwise, it has been found that the liquid reaction mixture obtained from the reaction of benzene with isopropanol to form cumene has a propene concentration of less than 1% by weight.

The cumene prepared by the process of the invention can be used directly for the preparation of phenol by the Hock process. However, it can also be advantageous to work up the reaction mixture obtained in the reaction of benzene with isopropanol or to recycle at least part of it to the reactor. The reaction mixture obtained can be worked up by, for example, separating the reaction mixture into organic and aqueous phases, e.g. in a phase separator. The aqueous phase and/or the organic phase can each be further subjected to an extraction. However, the phases obtained can also be passed to a distillation in which the various compounds are removed from the phases. The distillation can be carried out directly using the phases as they are obtained from the reactor or have previously been treated by extraction and/or phase separation.

Preference is given to separating the reaction mixture obtained from the reactor into an organic phase and an aqueous phase in a liquid/liquid phase separator like a decanter prior to distillation, in which case it can be advantageous to remove part of the heat energy from the reaction mixture before it enters the phase separator, e.g. by means of a heat exchanger. This embodiment is advantageous in that water is removed from the reactor effluent prior to distillation thereby reducing energy consumption. Additionally by applying this measure the water content of the recirculated portion of the reactor

effluent can be easily controlled to adjust the water content of the total feed stream into the alkylation reactor.

5 The aqueous phase can be worked up or disposed of. The work-up of the aqueous phase can comprise, for example, transferring the aqueous phase to a distillation apparatus in which an IPA-water azeotrope is separated from the remaining aqueous phase. The water-IPA azeotrope can be returned to the alkylation reactor.

10 The organic phase is fed to a distillation column in which cumene, by-products and starting materials are separated from one another. The starting materials which have been separated off can be returned to the reactor. It can be advantageous to  
15 return part of the organic phase and/or part of the aqueous phase of the reaction mixture without work-up to the reactor. The organic phase of the reaction mixture is preferably returned to the reactor in such an amount that the ratio of the recycled organic part of the reaction mixture to starting  
20 materials is from 1:1 to 100:1. It may be advantageous to remove part of the heat energy from the organic part of the reaction mixture which is recycled to the reactor by means of a heat exchanger. The recycle of the organic part of the reaction  
25 mixture can be achieved, for example, by means of a circulation line in which a pump is installed. The circulation line is preferably provided with a heat exchanger by means of which it is possible to influence the temperature of the organic part of the reaction mixture. The temperature of the recycled, organic  
30 part of the reaction mixture is preferably set so that the temperature of the mixture of recycled reaction mixture and starting materials corresponds approximately to the temperature at the reactor inlet.

The cumene separated off in the distillation column can be  
35 passed to work-up or further use in the Hock phenol process,

e.g. the oxidation. The by-products which have been separated off, for example polyisopropylbenzene or diisopropylbenzene, can be passed to further utilization or work-up. Such work-up steps can include, for example, transalkylation reactions in which the by-products can in large part be converted into cumene. The method of carrying out such transalkylation reactions is known to those skilled in the art.

#### Step II: Oxidation of cumene to cumene hydroperoxide

10

The oxidation of cumene to cumene hydroperoxide can be carried out in a manner known to those skilled in the art. For example, the oxidation can be carried out as described in EP 0 371 738. The oxidation of cumene is usually carried out at a temperature of from 60 to 150°C, preferably at a temperature of from 90 to 130°C. The oxidation of cumene is preferably carried out at a pressure of from 1 to 10 kg/cm<sup>2</sup>. The oxidation is carried out using molecular oxygen. This molecular oxygen can be supplied in the form of oxygen gas, air or a mixture of oxygen gas or air with an inert gas, e.g. nitrogen or a noble gas.

The gas comprising molecular oxygen is brought into contact with the cumene in the form of a cumene-containing solution. The contact between oxygen-containing gas and the cumene should be very intimate. This can be achieved in a manner known to those skilled in the art, e.g. by means of a bubble column reactor.

The cumene-containing solution preferably has a pH of greater than 2. The pH of the cumene-containing solution can be adjusted by addition of alkaline compounds to this solution. The pH of the cumene-containing solution can also be adjusted by work-up of the cumene used, e.g. by extraction of acidic constituents. As alkaline compounds, preference is given to adding aqueous solutions of sodium or potassium carbonate or

hydroxide. The addition of the alkaline compound to the cumene-containing solution is preferably carried out so that the pH of the cumene-containing solution does not go outside the pH range from 2 to 11 even as the reaction progresses.

5

An agent which initiates the oxidation reaction is preferably added to the reaction system. As initiators for the oxidation reaction, an azo compound such as  $\alpha,\alpha'$ -azobisisobutyronitrile or  $\alpha,\alpha'$ -azobis(cyclohexyl nitrile) can advantageously be added to the reaction system. However, cumene hydroperoxide can also be advantageously added as initiator to the reaction system. This has the advantage that no additional extraneous compounds are introduced into the reaction system. Preference is given to adding from 0.01 to 20% by weight of the initiator, based on the total weight of the starting materials, to the reaction system.

The oxidation of the cumene can be carried out continuously, batchwise or semicontinuously. The oxidation of the cumene to cumene hydroperoxide is preferably carried out continuously.

It can be advantageous for the reaction mixture obtained in the oxidation to be subjected to an after-treatment. The reaction mixture obtained in the oxidation is preferably concentrated so as to give a solution containing from 40 to 90% by weight of CHP, particularly preferably from 60 to 85% by weight of CHP. Concentration is preferably carried out by distillation of unreacted cumene from the reaction mixture.

Step III: Acid-catalyzed cleavage of cumene hydroperoxide into phenol and acetone

The process step of acid-catalyzed cleavage of cumene hydroperoxide can be carried out in a manner known to those

skilled in the art. The acid-catalyzed cleavage of cumene hydroperoxide is described, for example, in EP 0 589 588, US 4 016 213, DP 1 443 329, US 4 358 618, GB 930 161 or EP 0 371 738.

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The acid-catalyzed cleavage of cumene hydroperoxide (CHP) can be carried out homogeneously or heterogeneously. The cleavage of CHP is preferably carried out by homogeneous cleavage. As catalysts, it is possible to use strong acids such as sulfuric, 10 hydrochloric or hydrofluoric acid. It is likewise possible to use heteropolyacids. It is also possible to use solid catalysts, e.g. acidic ion exchange resins or acidic zeolites. If liquid acids are used, they are added to the reaction mixture comprising CHP. Preference is given to adding an acid 15 catalyst to the reaction mixture in such an amount that the content of acid catalyst is from 0.002 to 5% by weight.

The reaction mixture usually comprises not only CHP but also a solvent. Solvents which can be used are aromatic or aliphatic 20 hydrocarbons, e.g. cumene, benzene, hexane, heptane or cyclohexane, alcohols such as ethanol, methanol, propanol or isopropanol, or ketones or aldehydes, e.g. acetaldehyde, acetone, methyl isobutyl ketone. Preference is given to using phenol, cumene and/or acetone as solvent. The solvent content 25 of the reaction mixture in the cleavage reactor is from 1 to 25 times the CHP content.

The actual cleavage is preferably carried out in one or more 30 reactors. The temperature in this reactor or these reactors is preferably from 40 to 90°C. The reaction mixture which is taken from the reactor or reactors can be recirculated at least partly to the reactor inlet. Preference is given to recirculating at least 25-95% of the reaction mixture taken 35 from the reactor outlet to the inlet of the cleavage reactor or

reactors.

It may be advantageous to carry out a subsequent heat treatment subsequent to the actual cleavage. For this purpose, the  
5 reaction mixture obtained from the cleavage reactor is transferred to a tube reactor. The tube reactor is preferably at a temperature of from 80 to 100°C. The intention of the subsequent heat treatment is to cleave both CHP which has not been cleaved in the cleavage reactors and dicumyl peroxide  
10 (DCP) which may have been formed from CHP and dimethylbenzyl alcohol in the cleavage reactors.

The cleavage product mixture, which can come directly from the cleavage reactor or else from the subsequent heat treatment, is  
15 worked up by distillation. This work-up produces, in a first separation step, crude acetone which can be hydrogenated to give isopropanol. In further distillation steps, the desired phenol is isolated from the cleavage product mixture and can be passed to work-up or use. Unreacted cumene and compounds which  
20 may have been formed by secondary reactions, e.g. AMS, can be recycled to the overall process in a manner known to those skilled in the art.

#### Step IV: Hydrogenation of acetone to isopropanol

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The process of the invention or the process step according to the invention makes it possible to prepare isopropanol from acetone containing impurities, by hydrogenation of acetone. In particular, the process of the invention makes it possible to  
30 prepare isopropanol from crude acetone, e.g. crude acetone which is obtained in the acid-catalyzed cleavage of cumene hydroperoxide.

Typical impurities in crude acetone are, for example, water,  
35 cumene and/or acetaldehyde. Crude acetone containing up to 15%

by weight of impurities can be used in the process or process step according to the invention. Preference is given to using crude acetone containing from 2.5 to 13% by weight of impurities. Crude acetone to be used according to the invention  
5 can contain up to 5% by weight of water, 7.5% by weight of cumene and/or 3 000 wppm of acetaldehyde.

The hydrogenation not only converts acetone into isopropanol but also converts the cumene into hydrocumene and the  
10 acetaldehyde into ethanol. Depending on the purpose for which the isopropanol prepared according to the invention is to be used, these compounds can be separated from the isopropanol in a manner known to those skilled in the art.

15 The process of the invention or the process step according to the invention can be carried out in one or more stages. The process of the invention is preferably carried out in at least two stages. The process stages can be carried out individually, in parallel and/or in a cascaded manner. The process stages are  
20 preferably carried out in a circuit or tube reactor.

The hydrogenation of acetone is preferably carried out as a liquid-phase hydrogenation. The liquid-phase hydrogenation is preferably carried out at a temperature of from 60 to 140°C,  
25 more preferably from 70 to 130°C, and a pressure of from 10 to 50 bar, more preferably from 20 to 35 bar. In the various process stages, different temperature and/or pressure conditions can be employed.

30 The hydrogenation can be carried out using equimolar amounts of hydrogen and acetone. The hydrogenation is preferably carried out using an excess of hydrogen. The molar ratio of hydrogen to acetone is preferably at least 1:1. The hydrogenation is preferably carried out at a feed ratio of hydrogen to acetone  
35 of from 1:1 to 5:1, particularly preferably from 1:1 to 1.5:1.

Apart from the hydrogenation reactions, it is possible for further reactions in which acetone and/or isopropanol is consumed to occur, e.g. catalyzed by a catalyst. For example, alkali-catalyzed aldol condensation of acetone can form diacetone alcohol (DAA) which can be hydrogenated to hexylene glycol (HG). Elimination of water from DAA and hydrogenation of the mesityl oxide (MOX) formed by elimination of water can produce methyl isobutyl ketone (MIBK) which can be hydrogenated to give 4-methyl-2-pentanol (MPOL). The desired product isopropanol can react further by elimination of water to form diisopropyl ether (DIPE).

Since the occurrence of these secondary reactions decreases the yield of isopropanol based on the acetone used, the catalyst used should not promote these reactions. For this reason, a catalyst should ideally be neutral, i.e. not alkaline and not acidic.

Suitable catalysts for carrying out the process of the invention are commercial hydrogenation catalysts comprising Cu, Cr, Ru and/or Ni as active component on neutral support materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ , activated carbon and/or  $\text{ZrO}_2$ , or support materials comprising mixtures thereof. Particular preference is given to using nickel-containing catalysts comprising about 10% by weight of nickel on a neutral support. Suitable neutral support materials are, in particular,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and mullite.

The process of the invention is preferably carried out in at least two process stages, where the reactor of the 1st process stage is configured as a circulation reactor and the reactor of the 2nd process stage is configured as a tube reactor.

A major part of the conversion of acetone occurs in the circulation reactor. The circulation reactor is equipped with a

product recycle loop. The reactor preferably works at a high concentration level and can therefore be operated using a small circulation ratio. The ratio of circulated product stream to acetone fed in is from 0.5:1 to 20:1, preferably from 2:1 to 10:1. It can be advantageous to cool the reaction product from the circulation reactor. It is possible to cool both the substream of the reaction product which is recirculated to the reactor and also the substream which is passed to the 2nd process stage or the tube reactor.

10

The initial temperature of the 1st process stage is advantageously from 60 to 90°C, and the total pressure is from 10 to 50 bar. Depending on the initial activity of the catalyst, it may be advantageous to reduce the initial temperature or to increase the circulation ratio in order to set the desired outlet temperature, which may correspond to the inlet temperature of the tube reactor.

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Since the hydrogenation is an exothermic reaction, the temperature increases in the reactor, so that cooling may be provided in and/or downstream of the circulation reactor. The hydrogenation in the first process stage is preferably carried out at a temperature of from 60 to 140°C, preferably from 70 to 130°C, and a pressure of from 10 to 50 bar, preferably from 20 to 35 bar.

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To hydrogenate acetone which has not been reacted in the first process stage, the reaction mixture from the circulation reactor is passed to a tube reactor. Such a tube reactor can be, for example, a shaft reactor operated as a tube reactor.

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The 2nd process stage, which preferably has plug flow characteristics, is preferably carried out at a temperature of from 60 to 140°C, preferably from 70 to 130°C, and a pressure

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of from 20 to 50 bar.

The above-described catalysts or catalyst systems comprising catalyst and catalyst support can be used in both process stages. Preference is given to using a nickel-containing catalyst comprising about 10% by weight of nickel on a neutral support in both process stages.

Combining the process steps I to IV of the process of the invention makes it possible to prepare phenol from benzene and oxygen without obtaining the coproduct acetone. Thus, for example, it may be advantageous for the acetone formed in the cleavage of CHP in process step III of the process of the invention to be used at least partly in step IV in the hydrogenation of acetone to isopropanol as starting material. Since crude acetone can be used directly as starting material for the hydrogenation in process step IV of the process of the invention, costly work-up of the crude acetone, as is required in conventional processes, can be omitted. It is naturally also possible to use purified and/or purchased acetone in the hydrogenation. The isopropanol formed in the hydrogenation of the acetone or crude acetone can be used directly for the alkylation of benzene (process step I). However, it can likewise be advantageous for the isopropanol from step IV to be purified by suitable measures, e.g. a thermal work-up, before use in the alkylation. The thermal work-up can, for example, comprise purification of the isopropanol by distillation in two distillation columns, with low boilers being separated off in the first column and high boilers being separated off in the second column.

A person skilled in the art of phenol production will be able to see further possible combinations which are likewise subject matter of the present invention. Thus, it is possible to combine individual process steps according to the invention

with other advantageous process steps. Such combinations are also subject matter of the present invention.

Fig. 1 and Fig. 2 show two embodiments of the substep of the process of the invention in which isopropanol is prepared from crude acetone by hydrogenation. Fig. 3 and Fig. 4 show two embodiments of the overall process in which cumene is obtained from acetone and benzene.

Fig. 1 shows one embodiment of the process step of acetone hydrogenation in the process of the invention, without the process being restricted to this embodiment.

The feed F can be placed in the separation vessel A by means of the pump FP or can be fed in continuously in the case of continuous operation. From the separation vessel, the reaction mixture can be circulated by means of the circulation pump ZP either via the bypass bp or the reactor R in which the catalyst bed KB is located. The reaction mixture can be heated to the desired temperature by means of the heat exchanger K1. Hydrogen is introduced into the system via H. The reactor R is followed by a cooler K2 in which the reaction mixture can be cooled. After cooling, the reaction mixture goes to the phase separation vessel A. Product can be taken from the reaction system via P.

Fig. 2 shows a further embodiment of the process step of acetone hydrogenation in the process of the invention, without the process being restricted to this embodiment.

In this embodiment, a crude acetone stream a together with a hydrogen stream b1 is fed into a circulation reactor R1. The reaction mixture is conveyed from the circulation reactor via line c to a phase separation apparatus PT1. Unconsumed hydrogen is separated from the reaction mixture formed in the

circulation reactor by phase separation in the phase separator PT1. This hydrogen can be fed back into the circulation reactor via line rg1. The liquid part of the reaction mixture can likewise be recirculated at least partly to the circulation  
5 reactor via line ra. Heat can be introduced into or removed from the recirculated reaction mixture by means of the heat exchanger W1. Part of the liquid part of the reaction mixture can be conveyed via line d to a tube reactor R2, with the reaction mixture being brought to a particular temperature in a  
10 heat exchanger W2. The reaction mixture is conveyed together with hydrogen from line b2 to the tube reactor R2. The reaction mixture leaves the tube reactor via line e. After leaving the tube reactor via line e, hydrogen present in the reaction mixture is again separated from the liquid part of the reaction  
15 mixture by phase separation (e.g. by flashing off) in the phase separation apparatus PT2 and can be fed back into the tube reactor via line rg2. Via line f, the isopropanol formed by the hydrogenation of crude acetone is passed to further use.

20 Fig. 3 shows one embodiment of the process of the invention, without the process being restricted thereto.

In this embodiment of the process of the invention, a crude acetone stream a obtained in the cleavage of CHP is  
25 hydrogenated in a process step as described for Fig. 2 to form isopropanol which is obtained via line f. This is used for the alkylation of benzene to cumene.

For this purpose, the liquid phase from line f is fed into the  
30 reactor R3. Benzene is also fed into this reactor via line be. The alkylation takes place in this reactor. The reaction mixture from reactor R3 is transferred via line g and the heat exchanger W5 to the phase separation apparatus PT3. From this, an aqueous phase can be conveyed via line j to a work-up step

for the recovery of products of value, e.g. cumene or isopropanol dissolved in water, or to disposal. Via line *rb*, part of the organic phase of the reaction mixture can be recirculated to the reactor *R3*. Heat can be removed from or  
5 introduced into this recycled part of the reaction mixture by means of the heat exchanger *W3*. Part of the organic phase of the reaction mixture is conveyed via line *h* to the distillation column *K1*. At the top of the column, a product comprising predominantly benzene and/or isopropanol is taken off. Part of  
10 this can be fed back into the reactor *R3* via line *ri* or part of it can be removed from the system via line *i* and passed to another use or work-up. At the bottom of the column *K1*, a mixture boiling at a higher temperature than isopropanol is taken off and can be fed via line *k* into the side of the  
15 distillation column *K2*. At the top of the column *K2*, a cumene-containing fraction is taken off and this can be conveyed via line *cu* to further work-up or use, e.g. the oxidation. A fraction having a boiling point higher than that of cumene is obtained at the bottom of this column *K2*. This fraction can be  
20 fed via line *l* to the distillation column *K3*. In the column *K3*, polyisopropylbenzenes and/or diisopropylbenzenes are separated from high boilers. The multiply alkylated benzenes are taken off at the top of the column and conveyed via line *dib* to the reactor *R4*. High boilers are obtained at the bottom of the  
25 column *K3* and can be passed via line *hs* to work-up or use. In addition to the multiply alkylated benzenes, benzene is introduced via line *be2* into the reactor *R4* in which the transalkylation takes place. The reaction mixture leaving the reactor is fed via line *re*, in which the heat exchanger *W4* by  
30 means of which heat can be removed from or introduced into the reaction mixture is located, into the distillation column *K1*.

Fig. 4 shows a further embodiment of the process of the invention, without the process being restricted thereto.

In this embodiment of the process of the invention, the isopropanol is not, as shown in Fig. 3, fed directly to the alkylation but instead is firstly worked up and purified by distillation and subsequently fed to the alkylation reactor.

5 Unlike the embodiment shown in Fig. 3, the reaction mixture obtained in the phase separation apparatus PT2 or the liquid part of the reaction mixture is not conveyed directly to the reactor R3, but is instead conveyed via line f2 to the distillation column D1. In this, the isopropanol is separated

10 from low boilers. These low boilers, e.g. acetone, are taken off at the top of the column via line m and are passed to work-up. If the low boilers are mainly made up of acetone, this can be fed back into the reactor R1. The fraction taken off at the bottom of the column can be conveyed via line n to a further

15 distillation column D2. In this distillation column, isopropanol is separated from high boilers. The isopropanol taken off at the top of the column can be passed via line ri to the reactor R3 in which the alkylation reaction takes place as in Fig. 3. The high boilers separated off from the isopropanol

20 and obtained at the bottom of the column can be passed via line o to work-up or use.

#### Example 1: Hydrogenation of acetone (batchwise procedure)

25 In an experimental plant as shown in Fig. 1, the circulation reactor was charged with about 65 g of catalyst (10% nickel on  $\alpha$ -aluminium oxide). The feed F is placed in the separation vessel A and circulated by pumping via the bypass bp. The apparatus is subsequently brought to the desired temperature.

30 At the beginning of the reaction, the reactor R is switched to the circuit. After about 5 minutes, a constant temperature and a constant pressure have been established, and the first product samples are taken. The temperature was about 130°C and the pressure was 25 bar abs (partial pressure of H<sub>2</sub>: about

20 bar abs). Hydrogen was introduced via line H. Hydrogen was introduced automatically in an amount corresponding to that consumed by the hydrogenation. As feed, acetone containing the impurities shown in table 1 was initially placed in the separation vessel A. Table 1 likewise indicates the composition of the reaction mixture after the hydrogenation.

Table 1: Composition of the reaction mixture from example 1 before and after hydrogenation (DL = detection limit)

Amounts in % by mass	Before hydrogenation	After hydrogenation
Water	3.9	3.8
Acetone	94.3	0.08
Methanol	0.019	0.011
Isopropanol	< DL	95.0
Diacetone alcohol	< DL	0.023
2-Methyl-2,4-pentanediol	< DL	0.039
Acetaldehyde	0.09	< DL
Dimethoxymethane	< DL	0.001
Cumene	1.6	0.013
Hydrocumene	0.002	0.9

As can be seen from the table, the process step according to the invention is very suitable for preparing isopropanol from crude acetone.

Example 2: Hydrogenation of acetone to isopropanol which is subsequently used for the alkylation of benzene to cumene

In a plant as described in Fig. 4, crude acetone comprising 94% by weight of acetone together with water (about 4% by weight) and cumene (about 1.2% by weight) and also, at least, methanol, acetaldehyde, dimethoxymethane, hydrocumene, diacetone alcohol

and 2-methyl-2,4-pentanediol in amounts of about 100 wppm each is fed into the circulation reactor which is provided with a reduced and stabilized nickel catalyst (10% nickel on  $\alpha$ -aluminium oxide). In addition, a stream of hydrogen is fed into the circulation reactor. The circulation ratio was 2.5:1. The hydrogenation of the crude acetone in the circulation reactor is carried out at a temperature of from 60 to 140°C and a pressure of from 20 to 40 bar abs.

10 The reaction mixture taken from the circulation reactor was depressurized to separate off the hydrogen and was subsequently conveyed to a tube reactor into which hydrogen gas was likewise fed and which was likewise provided with a reduced and stabilized nickel catalyst. The after-hydrogenation of crude  
15 acetone which had not been hydrogenated in the circulation reactor occurred in this tube reactor which had a temperature profile of from 90 to 132°C and a pressure of from 20 to 40 bar abs. After separating off the hydrogen, the reaction mixture had the following composition: about 94% by weight of  
20 isopropanol, 0.5% by weight of acetone, 4% by weight of water, about 1.2% by weight of hydrocumene together with dimethoxymethane, methyl isobutyl ketone, diacetone alcohol, hexylene glycol, 4-methyl-2-pentanol and 2-methyl-2,4-pentanediol in the low wppm range. Cumene and acetaldehyde  
25 could no longer be detected in this mixture.

This reaction mixture was worked up by introducing it into a first distillation column in which the low boilers, e.g. acetone, methanol and dimethoxymethane, were separated from the  
30 reaction mixture at the top. The remaining reaction mixture was taken from the bottom of this column and fed into a further distillation column. In this distillation column, the isopropanol was separated from the reaction mixture and taken off at the top of the distillation column.

The isopropanol obtained in this way was fed directly into a circulation reactor into which benzene was also fed. The alkylation took place in this circulation reactor at a pressure of about 45 bar abs, and the reactor had a temperature profile of from 200 to 230°C. In a downstream phase separation vessel, the reaction mixture was separated into an organic phase and an aqueous phase. The aqueous phase, which is saturated with organic constituents, was distilled and the water-isopropanol azeotrope which was distilled off was recirculated to the circulation reactor. The organic phase from the phase separation vessel was partly recirculated to the circulation reactor, with the circulation ratio of recycled organic parts of the reaction mixture to starting materials fed into the reactor being 5:1. The other part of the organic phase of the reaction mixture was passed to three distillation columns connected in series. In the first distillation column, low boilers such as propene, benzene and unreacted isopropanol were separated off from the organic phase. These low boilers were fed back into the circulation reactor as alkylation reagent. The bottoms from this column were passed to the next column in which cumene was separated from the remaining organic phase. This cumene was fed directly to the oxidation for preparing cumene hydroperoxide (CHP). The bottoms from the distillation column were fed into the third distillation column in which diisopropylbenzene and/or polyisopropylbenzenes were separated from the remaining organic, high-boiling compounds. The bottoms were passed to thermal utilization. The multiply alkylated benzenes were conveyed to a tube reactor into which benzene was also fed. A transalkylation reaction was carried out at a temperature of about 220°C and a pressure of 40 bar abs in the presence of zeolites as catalyst to form cumene from benzene and multiply alkylated benzenes. The reaction mixture from this reactor was conveyed back to the first distillation column after the alkylation reactor so as to be able to separate unreacted benzene from the reaction mixture once again, then to

separate the cumene from the reaction mixture in the next distillation column and to feed it to the oxidation.

Example 3: Alkylation of benzene with isopropanol  
(discontinuously)

In a stirred tank reactor 881 g (85 wt-%) benzene was reacted for one hour with 156 g (15 wt-%) isopropanol in presence of 8g of the catalyst shown in table 2 at a temperature of 230°C and a pressure of 50 bar abs. The composition of the reaction product was analyzed by gas chromatography after termination of the reaction. The results are given in table 2.

Table 2: Composition of the reaction product of example 3

	Catalyst	
	H- $\beta$ -150 ( $\beta$ -Zeolith)	H-DAY-55 (Y-Zeolith)*
cumene	22.6 wt.-%	13.6 wt.-%
diisopropylbenzene	2.3 wt.-%	1,8 wt.-%
triisopropylbenzene	0.0 wt.-%	0.1 wt.-%
diisopropylether	0.06 wt.-%	0.06 wt.-%
cumene selectivity in respect of benzene	93.1 %	90.6 %
cumene selectivity in respect of isopropanol	71.2 %	42.4 %
benzene conversion	17.4 %	9.9 %

\* prior art catalyst

Example 3 demonstrates, that by using the catalyst according to the present invention in the alkylation step an improved cumene selectivity as well as an increased benzene conversion compared with the prior art catalyst could be achieved.

## Claims:

1. A process for the preparation of cumene by reacting isopropanol or a mixture of isopropanol and propene with benzene in presence of a  $\beta$ -zeolite catalyst having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than 10:1.
2. The process of claim 1, wherein the catalyst used is a  $\beta$ -zeolite having an  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio of from 20:1 to 200:1.
3. The process of any of the preceding claims, wherein the acidity of the catalyst is modified by surface addition of water.
4. The process of any of the preceding claims, wherein the water content of the total feed stream to the reactor does not exceed 5 wt.-% based on the weight of the total feed stream.
5. The process of claim 4, wherein the water content ranges from 0.1 to 5 wt.-%, preferably from 0.5 to 4.5 wt.-%.
6. The process of any of the preceding claims, wherein the molar ratio of benzene to isopropanol in the feed stream to the reactor is greater than 1:1.
7. The process of claim 6, wherein the molar ratio of benzene to isopropanol in the feed stream to the reactor for the reaction of benzene with isopropanol is from 3:1 to 10:1.
8. The process of any of the preceding claims, wherein the reaction is carried out at a temperature of from 100 to 300°C.
9. The process of any of the preceding claims, wherein the

reaction is carried out at a pressure of from 10 to 100 bar abs.

- 5 10. The process of any of the preceding claims, wherein the reaction is carried out in a stirred tank reactor, a trickle-bed reactor or a fixed-bed reactor.
- 10 11. The process of any of the preceding claims, wherein the reaction mixture is, after leaving the reactor, separated into an aqueous phase and an organic phase by liquid/liquid phase separation.
- 15 12. The process of claim 11, wherein part of the organic part of the reaction mixture is returned to the reactor.
13. The process of claim 12, wherein the ratio of the recycled organic part of the reaction mixture to starting materials is from 2:1 to 100:1.
- 20 14. The process of any of the preceding claims, wherein the reaction mixture has an n-propylbenzene concentration of less than 300 wppm, preferably less than 150 wppm.
- 25 15. A process for preparing phenol from benzene, which comprises the steps
  - I. preparation of cumene according to a process of any of claims 1-14,
  - II. oxidation of cumene to cumene hydroperoxide,
  - 30 III. acid-catalyzed cleavage of cumene hydroperoxide to give phenol and acetone and
  - IV. hydrogenation of acetone to form isopropanol,
- 35 16. The process of claim 15, wherein the isopropanol used is obtained by hydrogenation of acetone in at least two process stages.

17. The process of claim 16, wherein the acetone used is crude acetone.
- 5 18. A process for the hydrogenation of acetone to isopropanol in at least two process stages, wherein the acetone used is crude acetone.
- 10 19. The process of any of claims 16 to 18, wherein the hydrogenation is carried out as a liquid-phase hydrogenation at a temperature of from 60 to 140°C and a pressure of from 20 to 50 bar.
- 15 20. The process of any of claims 16 to 19, wherein the crude acetone contains up to 15% by weight of impurities.
21. The process of claim 20, wherein the crude acetone contains from 2.5 to 13% by weight of impurities.
- 20 22. The process of claim 20 or 21, wherein the crude acetone contains up to 5% by weight of water.
23. The process of any of claims 20 to 22, wherein the crude acetone contains up to 7.5% by weight of cumene.
- 25 24. The process of any of claims 20 to 23, wherein the crude acetone contains up to 3000 wppm of acetaldehyde.
- 30 25. The process of any of claims 16 to 24, wherein the acetone conversion in the hydrogenation is at least 99%.
26. The process of any of claims 16 to 25, wherein a catalyst comprising Ni, Cu, Ru and/or Cr on a neutral support is used for the hydrogenation.
- 35 27. The process of claim 26, wherein a nickel-containing

catalyst on an  $\alpha$ - $\text{Al}_2\text{O}_3$  support is used.

28. Use of a  $\beta$ -zeolite catalyst having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio greater than 10:1 in the alkylation of benzene with isopropanol or a mixture of isopropanol and propene.
- 5

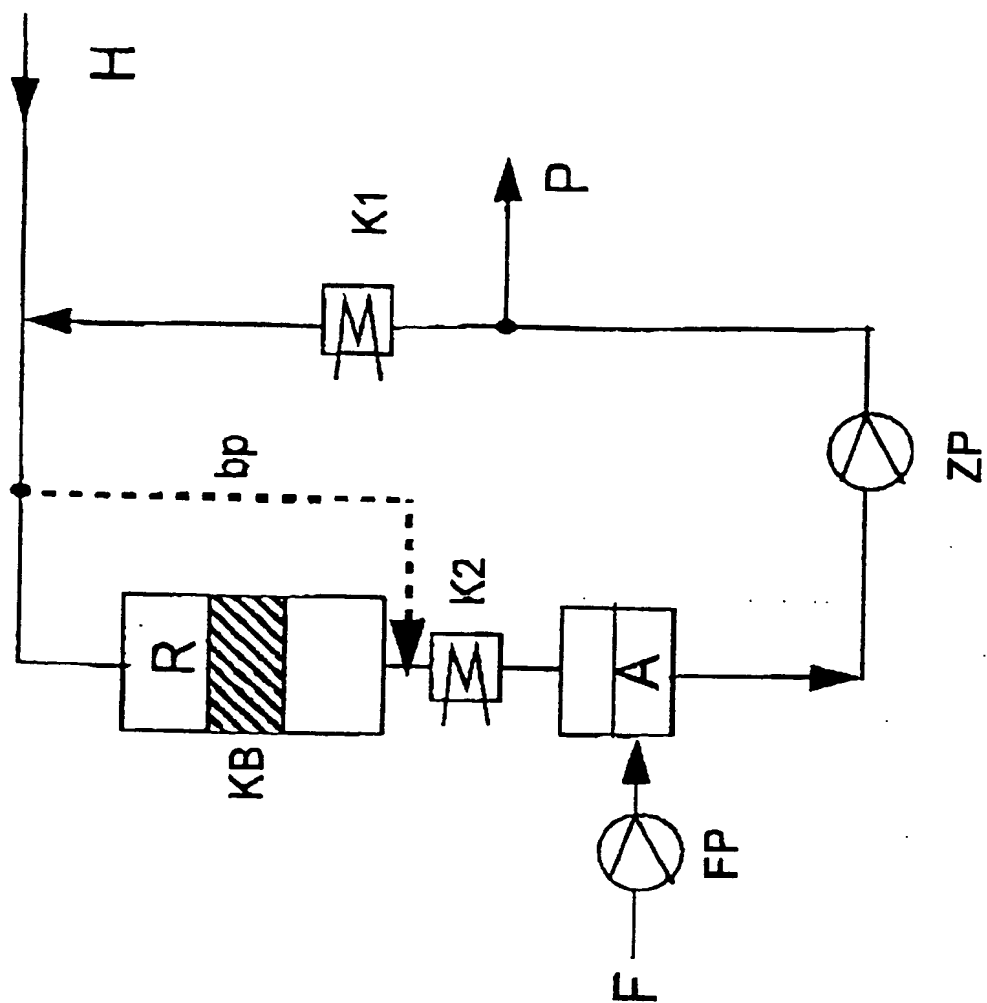


Fig. 1

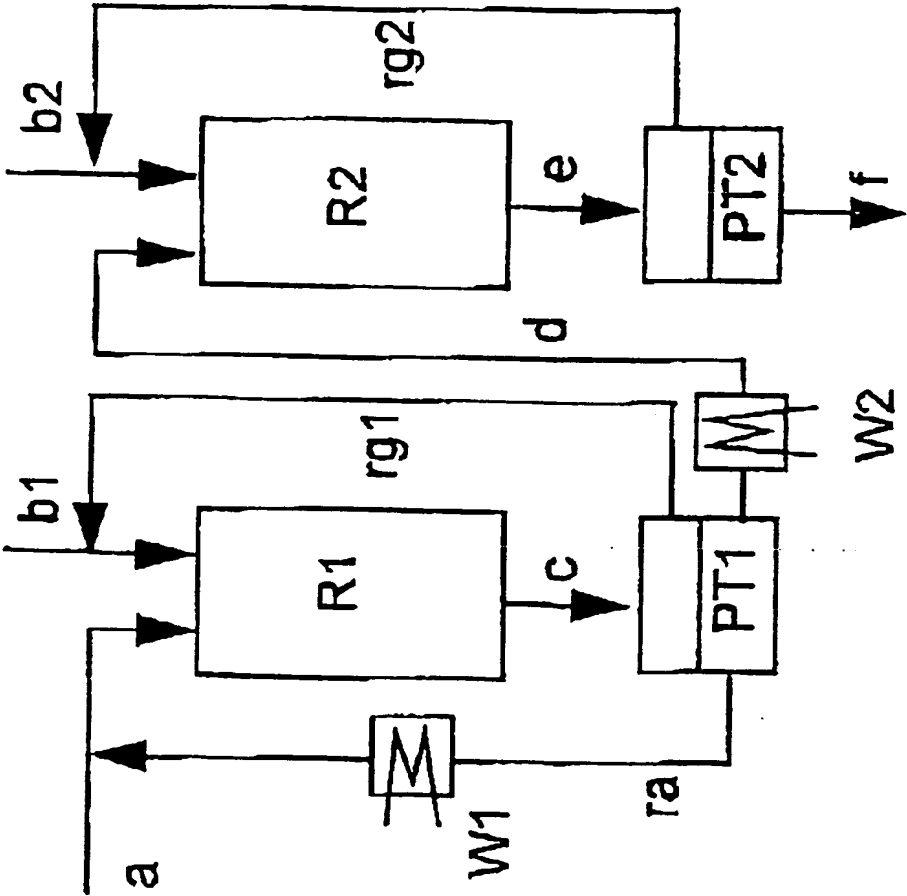
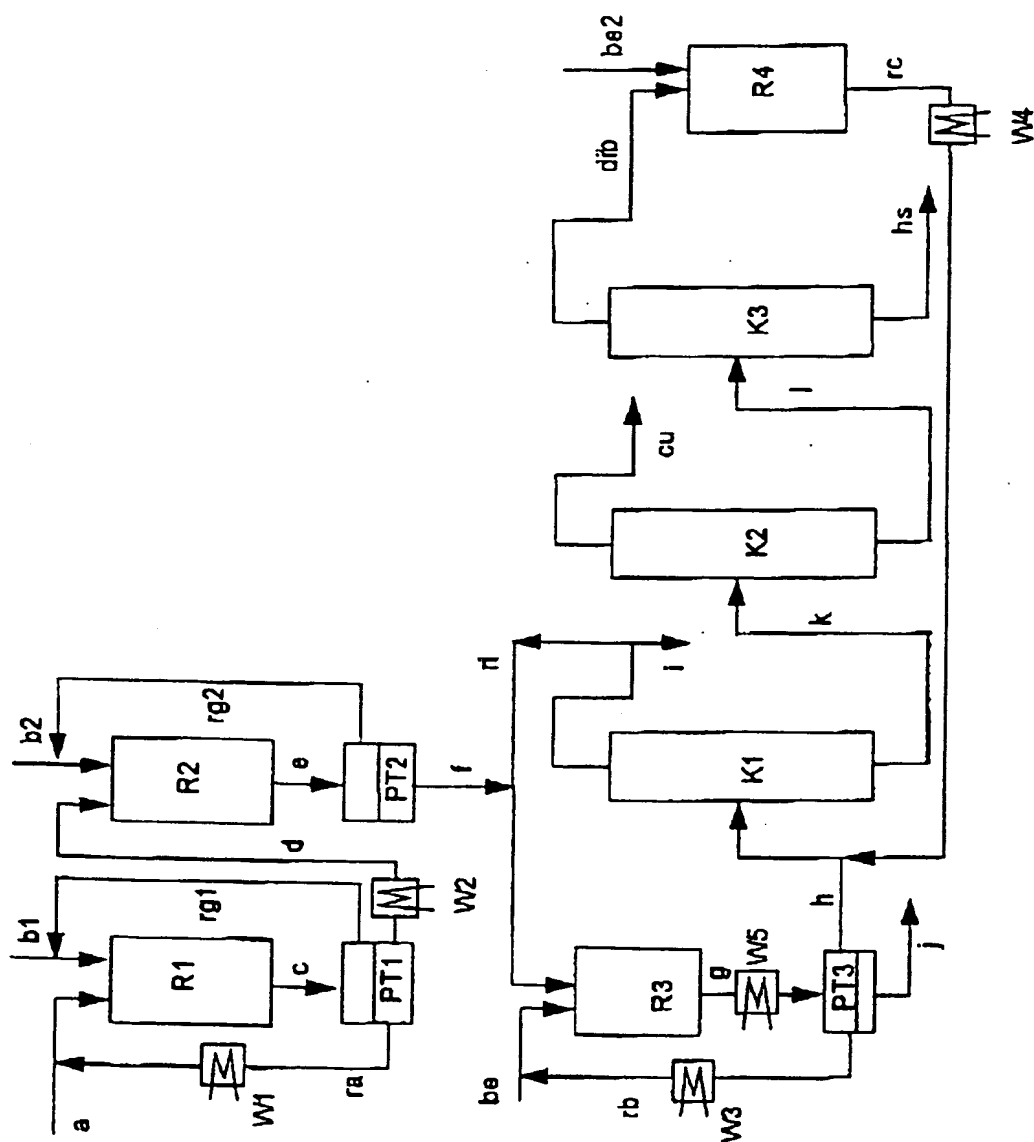


Fig. 2



**Fig. 3**

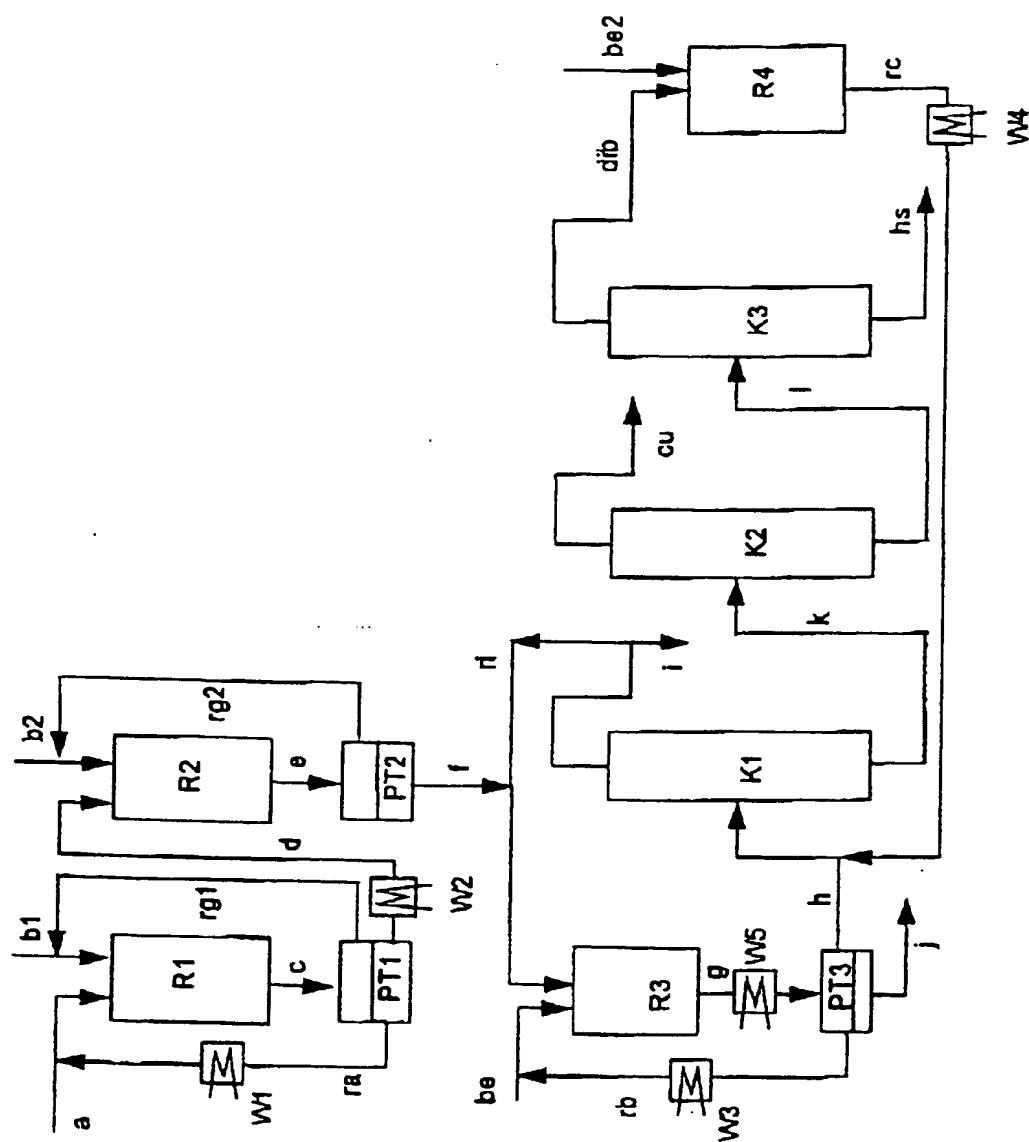


Fig. 3

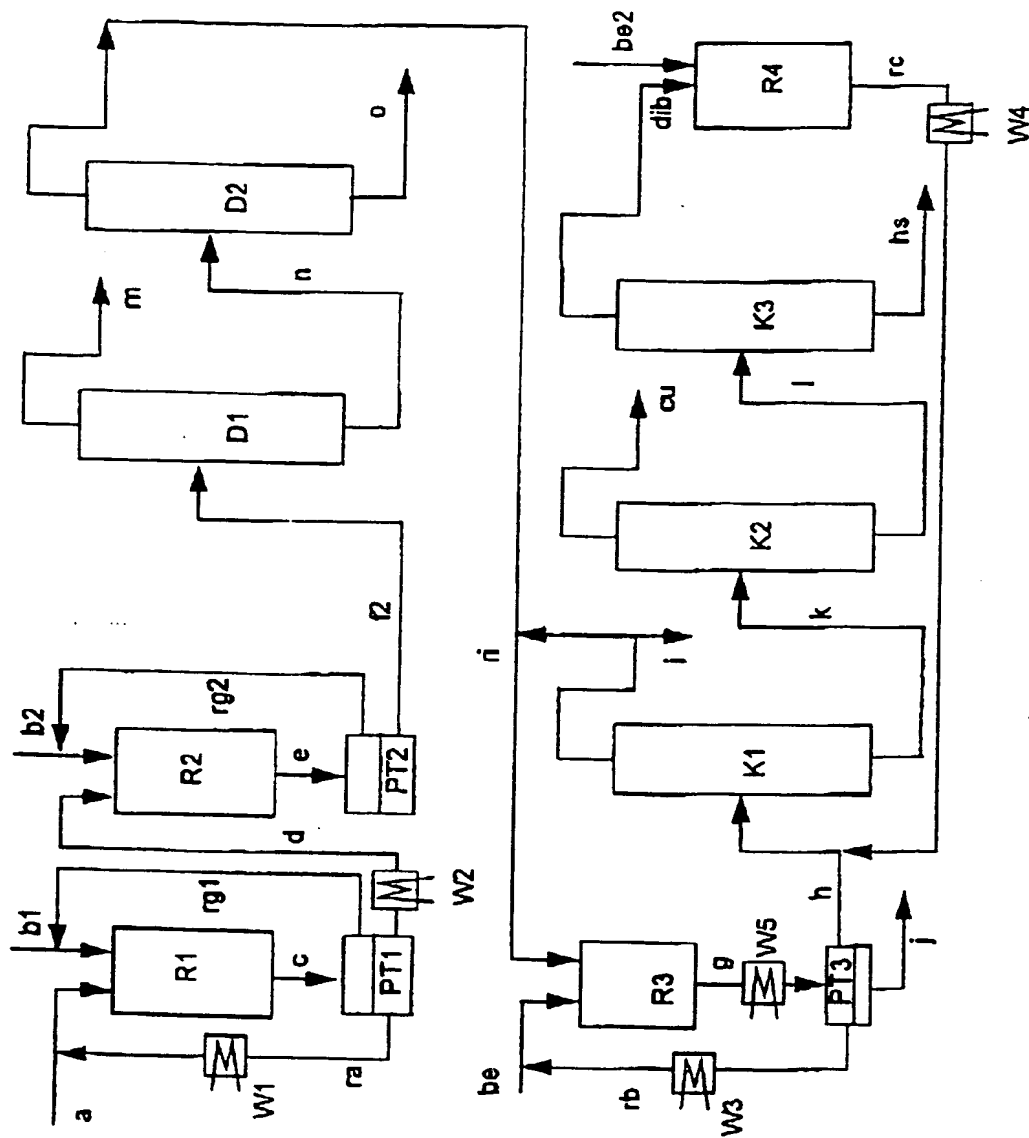


Fig. 4

## INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/EP 01/01797

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C15/085 C07C2/86 C07C39/04 C07C31/10 C07C29/145

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 538 518 A (COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH) 28 April 1993 (1993-04-28) claims	1-14
Y	EP 0 371 738 A (MITSUI PETROCHEMICAL IND) 6 June 1990 (1990-06-06) cited in the application claims	15
X	page 7	15-27
P, X	EP 1 069 100 A (ENICHEM SPA) 17 January 2001 (2001-01-17)	1-14
Y	claims	15



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/01797

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0538518	A	28-04-1993	NONE	
EP 0371738	A	06-06-1990	JP 2149534 A	08-06-1990
			JP 2593212 B	26-03-1997
			JP 2172927 A	04-07-1990
			JP 2603711 B	23-04-1997
			AT 102179 T	15-03-1994
			CA 2003925 A	28-05-1990
			CN 1043120 A, B	20-06-1990
			DD 334939 A	07-05-1992
			DD 301689 A	01-07-1993
			DD 344377 A	07-05-1992
			DD 344378 A	07-05-1992
			DE 68913448 D	07-04-1994
			DE 68913448 T	01-06-1994
			ES 2052030 T	01-07-1994
			JP 2231442 A	13-09-1990
			KR 149008 B	15-10-1998
			SG 20295 G	18-08-1995
			SU 1839668 A	30-12-1993
			US 5015786 A	14-05-1991
			RO 105956 B	30-01-1993
EP 1069100	A	17-01-2001	JP 2001055351 A	27-02-2001